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14. ABSTRACT

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15. SUBJECT TERMS

Benzoyl peroxide, cyclic organic peroxides,DART, hexa-methylene triperoxide diamine (HMTD), triacetonetriperoxide (TATP), ⌐|⌐−•TATP-d18⌐, triacetone triperoxide (TATP), time-of-flight–mass spectrometry (TOF–MS).

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have reported methods for their detection. Direct Analysis in Real Time is an emerging ambient pressure ionization technique in mass spectrometry (MS). This contribution presents the analysis, characterization and detection of triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) using DART.
Although typical experiments are done using helium, adding a small amount of ammonium hydroxide improved the detection limit to 30 ppb. This study also presents the detection and identification of benzoyl peroxide, tricyclopentanone triperoxide and tetramethylene diperoxide dicarbamide (TMDD) by MS and
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m/z 209.078 [M + H]+⌐ └└⌐ and small adduct peak at m/z 226.103 [M + H]+ that allowed its detection in standard solution and lab made samples. TMDD showed several peaks with a base peak at m/z 101.033, molecular peak at m/z 237.081 [M + H]+ └└⌐ and a strong ammonium adduct at m/z 254.108 [M + NH4+]+└⌐. All samples were analyzed by Raman Microscopy in order tocharacterize them and to confirm the MS results.

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Cyclic Organic Peroxides Characterization by Mass Spectrometry and Raman Microscopy

Alvaro J. Peña-Quevedo, James A. Laramee, H. Dupont Durst, and Samuel P. Hernández-Rivera

Abstract—Triacetone triperoxide and hexamethylene triperoxide diamine are among the most used and most studied non-nitro based high explosives. Still, there are other peroxides which do not have reported methods for their detection. Direct Analysis in Real Time is an emerging ambient pressure ionization technique in mass spectrometry (MS). This contribution presents the analysis, characterization and detection of triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) using DART. Although typical experiments are done using helium, adding a small amount of ammonium hydroxide improved the detection limit to 30 ppb. This study also presents the detection and identification of benzoyl peroxide, tricyclopentanone triperoxide and tetramethylene diperoxide dicarbamide (TMDD) by MS and Raman microscopy. TATP showed a single peak at *m/z* 240.144 $[M + NH_4]^+$ with the peaks at *m/z* 223.118 $[M + H]^+$ or 222.110 $[M]^+$ completely absent. Deuterium enriched $(TATP - d_{18})$ was analyzed for comparison. These presented a similar peak at *m/z* 258.267 $[TATP - d_{18} + NH_4]^+$. HMTD showed a peak at *m/z* 209.078 $[M + H]^+$ and small adduct peak at *m/z* 226.103 $[M + NH_4]^+$ that allowed its detection in standard solution and lab made samples. TMDD showed several peaks with a base peak at *m/z* 101.033, molecular peak at *m/z* 237.081 $[M + H]^+$ and a strong ammonium adduct at *m/z* 254.108 $[M + NH_4]^+$. All samples were analyzed by Raman Microscopy in order to characterize them and to confirm the MS results.

Index Terms—Benzoyl peroxide, cyclic organic peroxides, DART, hexa-methylene triperoxide diamine (HMTD), triacetone triperoxide (TATP), $TATP - d_{18}$, triacetone triperoxide (TATP), time-of-flight–mass spectrometry (TOF–MS).

I. INTRODUCTION

WIDESPREAD use of organic peroxides in terrorist acts has required government security agencies to evaluate new technologies for the detection of these compounds [1], [2].

Tri-acetone tri-peroxide (TATP) and hexa-methylene triperoxide diamine (HMTD) are the more commonly used cyclic organic peroxides in terrorist acts, such as the 2005 London bombing [3]. Several new methods have been developed for their detection at airports, government buildings and mass transportation facilities [1], [3]–[5].

In 1983, the first forensic analysis and characterization of TATP by electron ionization (EI) and chemical ionization (CI) mass spectrometry (MS) [5] was reported. Characterization of HMTD by x-ray analysis to determine its structure was published in 1985 [6]. Later in 1988, HMTD was fully characterized by nuclear magnetic resonance (NMR), Raman and infrared (IR) spectroscopies [7]. One of the first HMTD mass spectra was presented in 2000 [8]. In the same year, gas chromatography–mass spectrometry (GC–MS) based methodologies for TATP and diacetone diperoxide (DADP) detection at picogram levels were presented [9]. In 2001, a method for HMTD detection was described using high performance liquid chromatography–mass spectrometry (HPLC–MS) [10]. Later in the same year, the shoe-bomber case further motivated peroxide-based explosives detection [11]. In 2002, detection methods for TATP were described using HPLC separation, post column derivatization, MS analysis [12], and direct HPLC–MS analysis [13]. GC-electron capture detector (ECD) was used to observe TATP and HMTD decomposition products and these studies included essential thermal properties for further analysis by other techniques [14]–[16]. In addition, a theoretical proposition of a method for detection using metal cations was presented [17]. In 2003, a method for detection of TATP in air was developed [18]. This work was followed by a method to detect TATP using ion mobility spectrometry (IMS) [19]. A year later, TATP trace detection methods for GC–MS were performed using headspace analysis [20] and Solid Phase Micro Extraction [21]. Also in 2004, a method for TATP and HMTD analysis using HPLC–MS-MS was presented [22]. In 2005, methods for acetone peroxide analysis using GC–MS, GC-FTIR and Raman microscopy were discussed [23].

Due to novel advances in MS, 2006 witnessed a significant increment in studies of peroxide detection. A selected-ion flow-tube mass spectrometer was developed for TATP detection that provided 10 ppb detection levels [24]. The introduction of desorption electrospray ionization (DESI) was very useful for atmospheric pressure analysis of acetone peroxides reaching 15 ng detection limit but at a signal-to-noise ratio of only 20 [25]. Also, laser desorption–MS was used to analyze TATP, 2,4-dinitrotoluene (DNT) and 2,4,6-trinitotoluene (TNT) with 40 ppb detection levels [26]. Methodologies for TATP, HMTD, and other peroxides were developed using IMS, direct insertion probe MS and Raman scattering microscopy in pure form and

spiked with metal salts that could be present in the crude products [27], [28]. Later in the same year, several methodologies for TATP detection were compared: GC–MS with electron ionization (EI) and chemical ionization (CI) [29]. Positive ion CI was induced using ammonium ion to generate a molecular adduct at *m/z* 240. This method enabled the detection of picograms levels of TATP. Finally, the computational method proposed earlier was proven by electrochemical detection of HMTD and TATP using a Prussian-blue electrode [30]. In 2007, open-air chemical ionization (OACI)-TOF–MS was used to detect TATP, HMTD, and other peroxides, and the results were compared with EI [2], [31], [32]. The instrument used is commercially termed DART™ which is the contraction for "Direct Analysis in Real Time" used by JEOL-USA for OACI-MS. The heart of this technique is an ionizing jet of "metastable" helium that impinges on the sample to be analyzed. The ionization occurs at atmospheric pressure and ions of the material under analysis pass through an orifice and into a high resolution time of flight (TOF) mass spectrometer (MS). Recently, DESI was compared with desorption atmospheric pressure chemical ionization. The results showed that DESI formed adduct ions with Na^+, K^+ and NH_4^+ [33]. These multiple representations of the analyte complicate the interpretation of the spectrum. In addition, a simple method for TATP analysis using electrospray ionization (ESI) direct injection was presented to demonstrate fragmentation of TATP under these conditions [34]. Recent work focused on the analysis of TATP and its decomposition products by GC–MS using diluted sample insertion and solid phase micro extraction (SPME) [35].

This paper presents syntheses of cyclic organic peroxides, some of which are new and others were prepared for the study. Vibrational spectroscopy was used for characterization of known organic peroxides TATP, HMTD, benzoyl peroxide (BP), cyclopentanone triperoxide, and cyclic amide peroxide: tetramethylene diperoxide dicarbamide (TMDD). Raman spectroscopy was also used for purity check and in some cases as the only means for determining the success of the synthetic methods utilized. High resolution TOF measurements allowed peroxides to be identified even in complex mixtures. EI–MS and OACI–MS were compared and contrasted in organic peroxides characterization. Isotopic labeling experiments were used to help elucidate MS fragmentation mechanisms and assist in peak assignments for both MS and Raman spectroscopy spectra. One of the main contributions of this work is the validation of a fast, chemical preparation free, solventless methodology for home made explosives detection, including cyclic organic peroxides: OACI-TOF–MS was used as mass spectroscopic characterization tool and as a means of detecting these important chemical threats in ambient pressure *in situ* analysis mode.

II. PROCEDURES

A. Instrumentation

Vibrational characterization of cyclic organic peroxides was carried out using a Renishaw Raman Microspectrometer model RM2000 Renishaw, Inc. (Chicago, IL) equipped with CCD detector and Leica LM/LS microscope using an ultra long working distance $50\times$ objective. HMTD, TATP, TATP-d_{18}, TMDD and cyclopentanone triperoxide spontaneous Raman
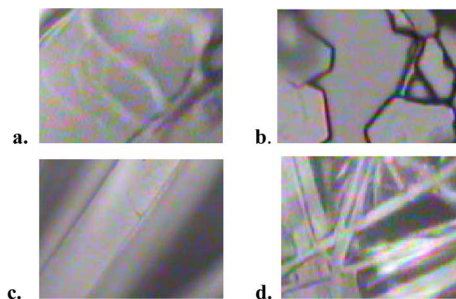

Fig. 1. White light images of sublimated peroxides ($50\times$ magnif.): (a) TATP; (b) cyclopentanone triperoxide; (c) HMTD; and (d) TMDD.

analysis was accomplished at excitation lines: 488, 514, 532, and 785 nm using laser power at sample of < 10 mW. The excitation sources were INNOVA 308 Ar^+ laser system wavelength selected for 488 nm blue line and 514.5 nm green line; VERDI-6 diode-pumped 532 nm laser with a variable output power of up to 6 W; and 899-01 Titanium/Sapphire ring laser operating at 785 nm pumped by the 532 nm laser (all laser systems from Coherent Laser Group, Santa Clara, CA.). Raman spectra were collected in the Raman Shift range of 100–4000 cm^{-1}, with three acquisitions and integration time of 10 s per scan. Dispersive Raman equipment was operated in confocal mode. Fourier transform infrared (FTIR) spectrometer used was a Thermo-Nicolet FT-IR spectrometer Nexus E.S.P with attenuated total reflectance (ATR) accessory and Bruker Optics model IFS 66 v/S FT-IR microscope.

An Agilent Technologies gas chromatograph model GC–MS 5890 GC system coupled to a 5790 mass selective detector was used in electron ionization (EI) mode-mass spectroscopy experiments. A JEOL GC-MateII direct probe system was also used to analyze by EI at 70 eV. A DART-TOF–MS (JEOL, USA, Inc., Peabody, MA) was used for the atmospheric pressure-CI–MS experiments.

B. Reagents

Chemical reagents used in this research included d_6-acetone (99% isotope), acetone, cyclopentanone, hexamethylene tetraamine, benzoyl peroxide (98% w/w), and formaldehyde (CH_2O, 37% wt), all obtained from Acros-Organics, Fairlawn, NJ. Hydrogen peroxide (H_2O_2, 50%) and urea (98% w/w) were obtained from Fisher Scientific International, Fairlawn, NJ. Hydrochloric acid (HCl, 12 M, VWR International, Inc., West Chester, PA) was used as catalytic agent. High purity acetonitrile *Omnisolv* (GC/HPLC/gradient analysis grade) was obtained from EMD Chemicals Inc., Gibbstown, NJ.

C. Preparation of Cyclic Organic Peroxides

HMTD and TATP, although commercially available as GC–MS standards (1 mg/mL), were synthesized to have a relatively large supply for the study. Recrystallized samples had lower impurities than commercial samples. Other cyclic organic peroxides were not commercially available and had to be synthesized and purified. White light images of TATP, cyclopentanone, HMTD and TMDD show well ordered crystals [Fig. 1(a)–(d)].
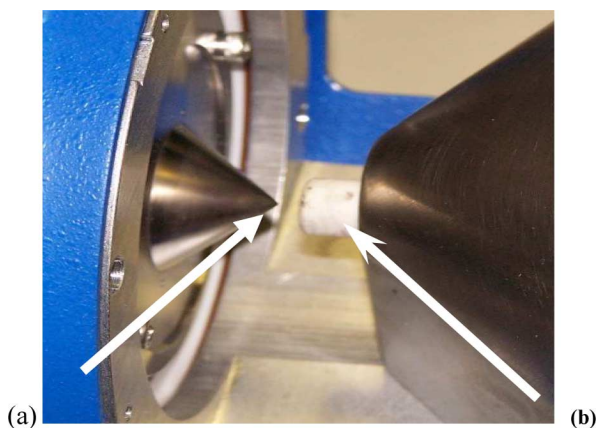
Fig. 2. Ambient pressure ionization zone in the DART/AccuTOF system: (a) ambient pressure inlet to the time-of flight mass spectrometer; (b) exit of CI gas and ionization region.

Fig. 3. Raman spectra of: (a) TATP and (b) d_{18}-TATP.

D. TATP, d_{18} TATP and Cyclopentanone Triperoxide

TATP, d_{18}-TATP and cyclopentanone were synthesized following Wolffstein's original procedure [36]. The reaction mixture as crystallized by ether evaporation and then purified by sublimation at a constant temperature of 80 °C.

E. Hexamethylene Triperoxide Diamine, HMTD

HMTD was synthesized following the method used by Von Girsewald [37]. The crystals were filtered out and washed with water. Due the low yield of the preparation, no purification was performed.

F. Tetramethylene Diperoxide Dicarbamide, TMDD

TMDD was prepared using Von Girsewald and Siegens method [38]. After three days of standing at 0 °C in a refrigerator, a white powder-like substance was obtained. This precipitate was filtered with a Büchner funnel and washed with distilled water. The crude product was allowed to dry and recovered.

G. Ambient Pressure Chemical Ionization MS Analysis

Stock solutions of 1.0 mg/mL of TATP, d18-TATP, BP, HMTD, and TMDD were prepared in acetonitrile. The sealed end of a capillary tube was dipped into the solutions and placed in the ambient pressure ionization zone (Fig. 2). Quantitative measurements were made using a 2 μL micropipette to aliquot an accurate amount of sample onto the capillary. Ammonium hydroxide can be used as an adduct forming agent in some types of compounds [31]. The use of NH_4^+ as an adduct formation promoter is routinely used for CI–MS analysis of ketones, acids, alcohols, and other oxygen-rich compounds such as peroxides and ethers [29], [39]. The effect of addition of a source of ammonium ions was investigated for organic peroxides studied.

III. RESULTS AND DISCUSSION

A. Raman Spectroscopy

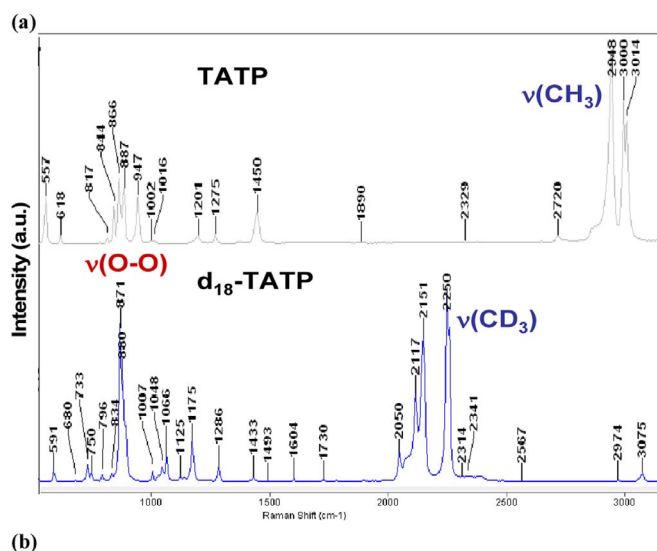Raman spectroscopy is an ideal technique for characterizating peroxides. The oxygen-oxygen bond vibration is unique to the peroxide moiety since it defines its chemical structure. These vibrations occur at 1000 cm^{-1}, 880 cm^{-1}, and 870 cm^{-1}. These same bands were also observed for cyclopentanone triperoxide. The large vibrational shift of the methyl groups upon substitution of CH$_3$ for the CD$_3$ moiety was used to differentiate TATP from d_{18}-TATP. The higher mass of the deuterium atoms causes the methyl stretching to shift from 3000–2700 cm^{-1} for TATP to 2300–2000 cm^{-1} for d_{18}-TATP (Fig. 3). Using these data, the degree of deuterium isotope incorporation was estimated at 99 atom %.

HMTD and TMDD exhibited similar methylene vibrational bands ca. 2990–2830 cm^{-1}. Characteristic peroxide bands were observed in the range of 980–900 cm^{-1} and near 770 cm^{-1}. Our HMTD results compare well with previous results [7]. No reference data for TMDD was found. The principal evidence of the synthesis of a carbamide compound is the strong absorption of the N-H stretching at 3336 cm^{-1} in FTIR absorption and 3346 cm^{-1} in Raman scattering [40], [41]. Urea has a strong carbonyl absorption in the range of 1700–1600 cm^{-1}; TMDD also showed the presence of this vibrational signature.

In the IR spectra, strong absorptions in the range of 1500–1660 cm^{-1} demonstrate the presence of a carbonyl group. The corresponding Raman signal was observed about 1650–1770 cm^{-1}. Characterization of the nitrogen-carbon bond present in amides can be observed at 1253, 1296, and 1127 cm^{-1} $\{\nu(N - C)\}$. These results not only verify that TMDD was prepared but predicts a possible structure for it.

B. GC–MS

GC–MS using electron impact ionization is a common analytical technique. A weak molecular ion is produced for the fragile TATP molecule. (Fig. 4), and abundant fragment ions at *m/z* 117 $[C_5H_9O_3]^+$, 101 $[C_5H_9O_2]^+$, 75 $[C_3H_6O_2]^+$, 59 $\{C_3H_7O\}^+$, 58 $[C_3H_6O]^+$ and a base peak at *m/z* 43 $[C_2H_3O]^+$ were observed.

The identity of the fragment ions is supported by predicted mass shifts for the d_{18}-TATP analog, these are *m/z* 126 $[C_5D_9O_3]^+$, 110 $[C_5D_9O_2]^+$, 82 $[C_3D_7O_2]^+$, 66 $\{C_3D_7O\}^+$,
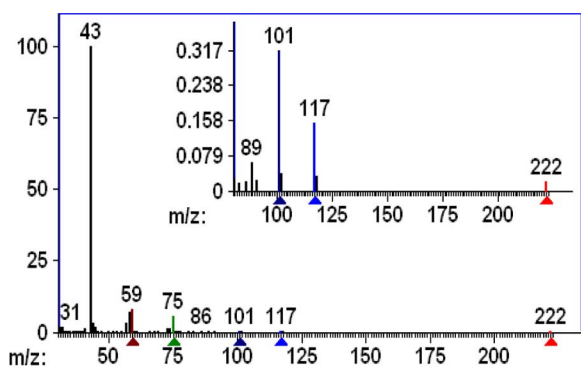
Fig. 4.   Mass spectrum of TATP by EI–MS. Inset: zoom high mass end region.

Fig. 5.   Mass spectra of d_{18}-TATP by EI–MS EI.

Fig. 6.   Benzoyl peroxide mass spectrum by API-TOFMS at 150 °C.
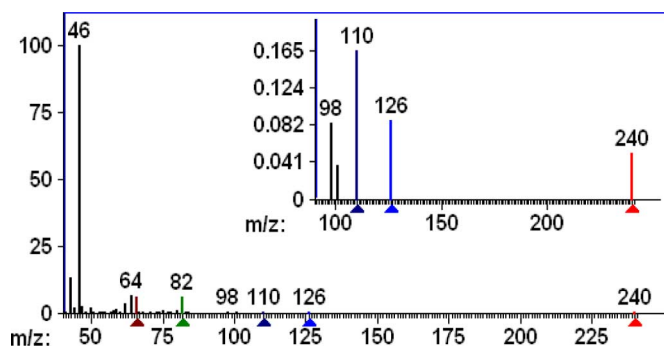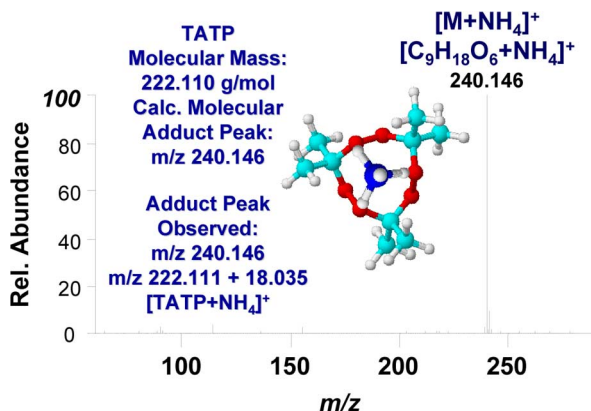

Fig. 7.   Mass spectrum of pure TATP by APCI at 200 °C.

64 $[C_3D_6O]^+$ and the base peak at m/z 46 $[C_2D_3O]^+$ (Fig. 5). The presence of these fragments together with the Raman results was used to characterize and verify the synthesis of TATP and of d_{18}TATP. GC/MS also showed a single peak in the chromatograms which confirms its purity.

On the other hand the low vapor pressure of HMTD impedes a determination of its purity by GC methods, which are overcome using a direct insertion probe. HMTD showed a strong molecular ion at m/z 208 and compares well with literature results [8], [15]. Fragment ions were seen at m/z 176 (loss of oxygen molecule) and m/z 88. Other typical fragments were observed at m/z: 149, 117, 112, 104, 73, 59, 58, 45 $[CH_2NO]^+$, 42 $[CH_2NCH_2]^+$, 32, 31, and 30 $[CH_4N]^+$.

C. Cyclic Ketone Peroxides and Benzoyl Peroxide

Some of the organic peroxides studied did not produce molecular peaks of significantly intensity when ionized with the APCI source. Instead, the formation of an adduct peak with ammonium was observed. To increase the molecular adduct peak signal in these peroxides, aqueous ammonium hydroxide was placed in the ionization region. This simple improvement enhanced the production of peroxide molecular adduct ions, even at relatively high temperatures (200 °C).

Benzoyl peroxide (BP) was analyzed by ambient pressure ionization–MS because it is commercially available and it is extensively used in medical treatments. BP has a molecular mass of 242.06 g/mol. API–MS produced a strong peak at m/z 260.09 $[BP + NH_4]^+$ (Fig. 6). The next peak of significant intensity was located at m/z 216.106 could be observed under certain conditions. This signal can be assigned to $[M + NH_4-CO_2]^+$. By
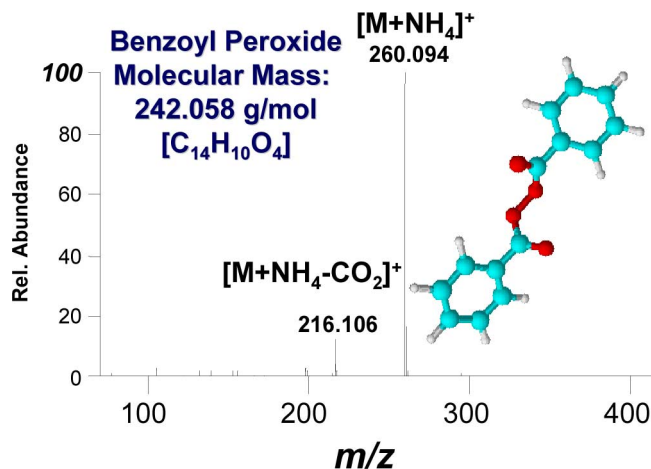
changing the temperature of the ionization chamber additional fragmentation was observed.

TATP was analyzed at different temperatures and in contrast with GC/EI–MS that requires low detector temperatures, API–MS analysis with NH_4OH vapor produced the molecular adduct at 200 °C, above TATP flash point at 150 °C. Fig. 7 shows the mass spectrum of TATP which presents a molecular adduct at m/z 240.146 $[TATP + NH_4]^+$. No molecular peaks were observed at m/z 222.110 $[TATP]^+$ or at m/z 223.118 $[TAPT + H]^+$. These results indicate that ammonium hydroxide stabilized the ionization of TATP and increased its detection. This property was also observed when d_{18}-TATP was analyzed by API–MS. A strong peak was observed at m/z 258.258 $[d_{18} - TATP + NH_4]^+$ with complete absence of signals at m/z 240.223 $[d_{18} - TATP]^+$ and at m/z 241.231 $[d_{18} - TATP + H]^+$ (Fig. 8)

Cyclopentanone triperoxide showed also a similar behavior as TATP, at m/z 318.190 $[M + NH_4]+$ (Fig. 9). m/z 059 belongs to an ion that is ascribed to an oxidized form of cyclopentanone, $[C_5H_9O_2]+$. This peak can be attributed to a contaminant or a decomposition product of the peroxide studied.

D. Amine and Amide Peroxide: HMTD and TMDD

HMTD has low solubility in most common solvents used and very low vapor pressure, which limits analysis by GC. It
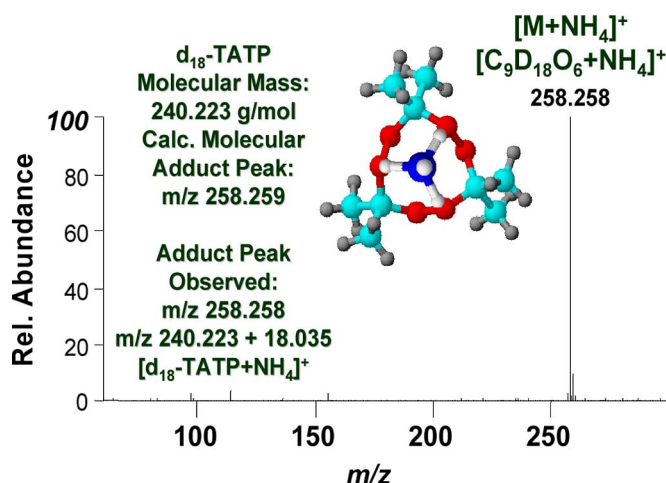
Fig. 8. Mass spectrum of d_{18}-TATP at 200 °C using ambient pressure ionization MS.
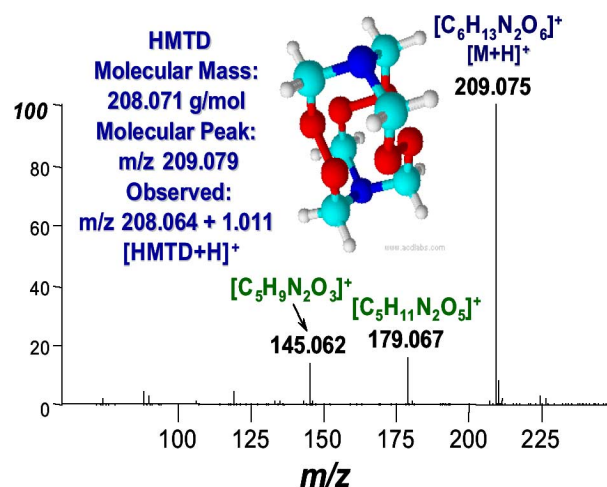

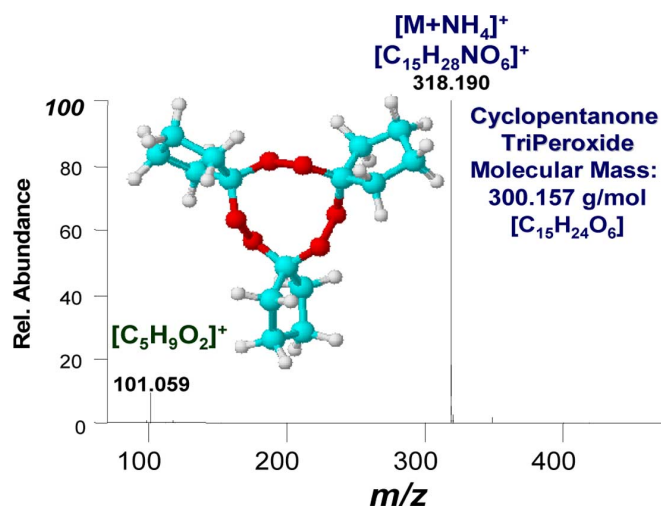Fig. 10. API-TOF–MS spectrum of HMTD at 150 °C.

Fig. 9. OACI-TOF–MS spectrum of cyclopentanone triperoxide.

is slightly soluble in chloroform, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). TMDD is insoluble in most organic solvents. This hampers most chromatographic analysis, including GC and HPLC. API-TOF–MS provided an excellent method for detection with considerably low detection limits. HMTD does not require ammonium hydroxide to promote the observation of the molecular ion, but adding NH_4OH solution increases the intensity of $[M + H]^+$ helping to identify this peroxide compound by chemical ionization.

Fig. 10 presents HMTD mass spectrum by API-TOF–MS with molecular mass at m/z 209.078 $[HMTD + H]^+$. Other significant mass fragments observed in lower abundance were located at m/z 226.104 $[M + NH_4]^+$, the adduct ion; m/z 179.067 $[C_5H_{11}O_5N_2]^+$, loss of formaldehyde; m/z 145.062 $[C_5H_9O_3N_2]^+$, loss of hydrogen peroxide; and m/z 88.040 $[C_2H_6O_2N]^+$. These peaks are constant at different ionization chamber temperatures, but intensities were different as the temperature increased. The optimal temperature for HMTD analysis by API-TOF–MS was found to be 150 °C. In the presence of ammonium hydroxide it was possible to observe the strong molecular ion at even at 200 °C.

Initially, TMDD required a higher ionization port temperature to detect the MS spectrum. Mass spectrum was optimally collected at inlet port temperature of 180 °C, close to its melting point. At this temperature TMDD showed the molecular peak at m/z 237.085 $[TMDD + H]^+$, similar to HMTD, but considerable fragmentation was also observed. After the first mass spectrum was obtained and confirmed using different ionization port conditions including using NH_4OH to generate NH_4^+ dopant, it was possible to lower the inlet port temperature to 150 °C showing an ammonium ion adduct peak $[M + NH_4]^+$ at m/z 252.111. When NH_4^+ vapor was added, TMDD behaved similar to TATP, showing a strong molecular adduct ion [1]. Fig. 11 shows TMDD mass spectrum with API-TOF–MS at low inlet temperature (150 °C). Even at this low temperature considerable fragmentation was observed with peaks at m/z 189.062, 175.083, 161.068, 146.058, 130.062, 118.061, and 102.069. To our knowledge, these results represent the only reported method of analysis for TMDD characterization and detection. Other MS analysis methods were tried including GC/EI–MS and HPLC/ EI–MS and direct insertion probe EI–MS, but results were limited by the low solubility of TMDD in the solvents tested and its extremely low vapor pressure.

E. TATP and HMTD Mixture Analysis

The soft chemical ionization that promotes the formation of the molecular ion or its adducts accompanied with minimum fragmentation, in most cases, combined with high mass resolution of the reflectron TOF allowed identification of mixtures of peroxides and differentiation of fragments with possible interferences. When a sample of TATP was placed in the APCI stream it was common to observe a peak at m/z 223.097, that was wrongly assigned to $[TATP + H]^+$. This peak is a typical environmental contamination due to diethyl phthalate that can be confirmed by its mass fragments of m/z 152.020, 100.077, 77.027, and 59.053. This problem was corrected by placing NH_4OH in the ion stream so that the ammonium adduct of TATP was observed and assigned correctly.

A mixture of HMTD and TATP gave the expected molecular ions at m/z 240.146 $[TATP + NH_4]^+$ and 209.079 $[HMTD + H]^+$ (Fig. 12). These results show that HMTD and TATP are

Fig. 11. Mass spectrum of TMDD at 150 °C.
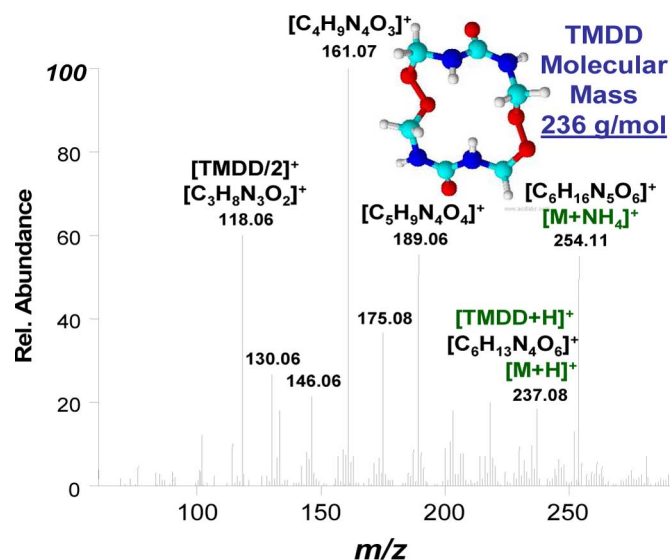

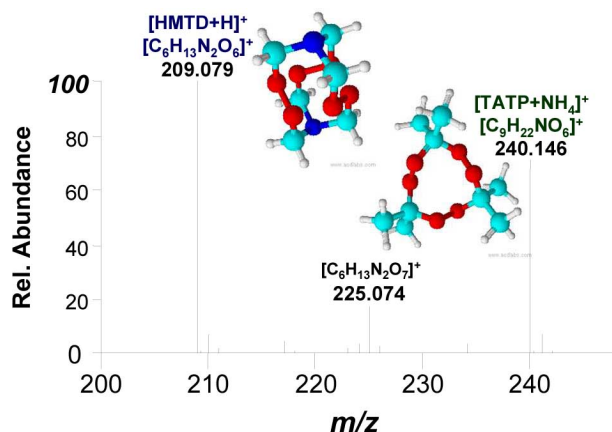Fig. 12. Mass spectrum of HMTD and TATP mixture.

ion source coupled with the high mass accuracy of the AccuTOF mass spectrometer allowed rapid and accurate determination of the peroxide explosives. In contrast, other chromatographic based methods coupled to mass spectrometric detection require a factor of $100\times$ longer analysis time.

TATP and HMTD ionize by different CI mechanisms to produce different types of molecular ion adducts, even when both chemicals are ionized simultaneously *in situ*. In the case of TMDD, the formation of both types of molecular ion adducts was observed, although the adduct form with NH_4^+ was more intense. In contrast to other organic peroxides analyzed by OS–MS, TMDD produced profuse fragmentation. Some TMDD fragments were identified. The possibility of achieving parts-per-billion to parts-per-trillion detection levels without sample preparation in open air sampling makes OA–MS an attractive technique for defense and security applications.

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ionized by different mechanisms. This is useful because the analyte is detected without regard to ionizing preparation conditions. This is not the case with other ionization techniques, such as DESI. There both compounds share a similar behavior regarding the type of adducts generated, and it depends upon the preparation conditions rather than on the analyte.

Although quantitative assessment of detection limits for TATP and HMTD was not done, an estimate of the detection capability for both compounds was obtained by diluting a 350 ppm stock solution mixture of the explosives by a factor of 10 and transferring two microliters to the sampling capillary tube. This corresponded to 70 pg of TATP and HMTD and resulted in a signal to noise ratio (S/N) of $> 10 : 1$. Experiments for lower detection limits are in progress but somewhat hindered by the fast decomposition of HMTD and the increase in the relative abundance of the fragments ions at *m/z* 179 and 145.

IV. CONCLUSION

A method for detecting organic peroxide explosives using ambient pressure chemical ionization–mass spectrometry (API–MS) was presented. The high speed analysis of DART

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